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Some kinetic properties of hydrogen corrosion in polycrystalline plutonium

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INTRODUCTION: In this study, an infrared (IR) pyrometer camera was used to map the dynamic temperature profiles produced by the growth of hydride sites on PuO_2-coated Pu. The effect of Pu surface orientation on heat transfer and hydriding reaction rate was investigated and the emissivities of oxide- and hydride-coated surfaces were measured. As the results of experimental analysis and thermal modeling, a fundamental reassessment of the hydriding process is necessary because of the existence of PuH_x where $x < 2$ during the corrosion process.

EXPERIMENTAL METHODS: Hydriding experiments were performed on Pu coupons cut from a 0.8mm thick sheet of PuO_2-coeated polycrystalline delta-phase Ga alloy. During a typical hydriding experiment, the test specimen was mounted in a two-piece aluminum holder fitted with a pair of indium o-ring seals pressed against the perimeter of the Pu sample surface [1]. The mounted sample was then placed in a massive aluminum block set inside an evacuable stainless steel chamber equipped with a turbomolecular pump, type K thermocouples, capacitance manometers, and sapphire windows for pyrometric imaging with an IR camera (Merlin Indigo, FLIR systems, Inc.). The emissivities of oxide- and hydride-coated Pu were obtained by adjusting the emissivity values in the software of the pyrometer camera at known temperatures such that there was agreement between thermocouple readings and pyrometer outputs. In the temperature mapping experiments, some coupons were mounted vertically, some at a 45^o inclined angle inside the reaction chamber. Since meaningful correlation among the results is contingent on confinement of

reaction to a single site, measurements were facilitated by scribing the oxide surface near the center of each PuO_2-coated sample [1].

RESULTS & DISCUSSION: The measured emissivities of PuO_2-, Pu_2O_3-, and $PuH_{2\pm x}$- coated Pu at normal incidence are 0.63, 0.65, and 0.90, respectively. Chronological sets of thermal images for the vertical and inclined samples were obtained. It is observed that reaction preferentially initiated at the scribed sites after rapid pressurization of the evacuated reaction chamber (10^{-4} Pa) with a 10.5 mmol of research grade H_2 at room temperature (296 $\pm$ 1 K). In both mounting positions, the appearance of additional reaction sites after the first few minutes shows that hydriding inherently nucleates due to the presence of impurities, defects, or other features that promote nucleation [1]. However, the member of the secondary nucleation sites on inclined samples consistently exceeded the corresponding number for vertical samples by a factor of 4-5. The appearance of additional secondary sites on inclined samples after coincided with the point at which ejection of hydride particles from the reaction site was observed. This suggests that nucleation is promoted by the deposition of spalled hydride particles onto the oxide-coated Pu surface. That conclusion is consistent with facile autoreduction of PuO_2 layer to catalytic Pu_2O_3 at elevated temperatures attained by localized heating of the oxide by hot particles and by their continuing reaction with H_2. The hydride debris/powder started out as thermally hot $PuH_{2\pm x}$ with $2 \pm x < 3$ and continued to react with H_2 to form PuH_3, releasing more heat [1]. However, in the vertically mounted position, most of the hot and reacting $PuH_{2\pm x}$ debris/powder fell off the coupon under the force of gravity, carrying with it much of the heat. So, the temperature rise associated with hydriding corrosion varies according to the orientation of the Pu coupon. Experimentally, the temperature rise was only a few degrees in the first few minutes of reaction, but eventually reached a maximum ΔT of 60K and 105K for the vertical and inclined samples, respectively. Interestingly enough, thermal imaging showed that hydriding reaction continued strongly for a few more minutes after most of the hydrogen in the gas phase has been consumed. In addition, heat-transfer thermal modeling of the hydriding reaction [2] reveals that the heat released during the first few minutes of the reaction were substantially less than that cited for PuH_2 formation [3]. These findings are, however, consistent with a hydriding reaction model in which grain boundary diffusion and reaction are much faster than grain reaction.

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[2] COMSOL Multiphysics version 4.2a, by COMSOL Inc., Stockhom, Sweden